

# Disentangling bulk and surface contribution in correlated systems and buried interfaces

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## Outline

- VOLPE project: Characteristics and Performances
- Results:
  - Transition Metal Oxides (Ruthenates)
  - Enhanced s-contribution @ Fermi level ( $In_2O_3$ ,  $PbO_2$ )
  - Buried interfaces (spin valve interface, diluted magnetic semiconductors)
- Conclusions and perspectives

# VOLPE's history

## (VOLume PhotoEmission from solids with Synchrotron Radiation)

Operational since 2005 at ESRF (ID16 beamline)

EU project funded in 2001 – Trieste, Univ. Rome III, ESRF, EPFL, LURE

Long Term Proposal till 2008 + **Open to users**

“Bulk sensitive Photoemission on highly correlated materials”

C. S. Fadley, Univ. Davis, US

M. Grioni, EPFL, Switzerland

J. Joyce, Los Alamos, US

O. Tjernberg, RIT, Sweden

L. H. Tjeng, Univ. Köln, Germany

Core levels + Valence band

Kinetic energy up to 6-10 keV

Statistics comparable to LE-PES

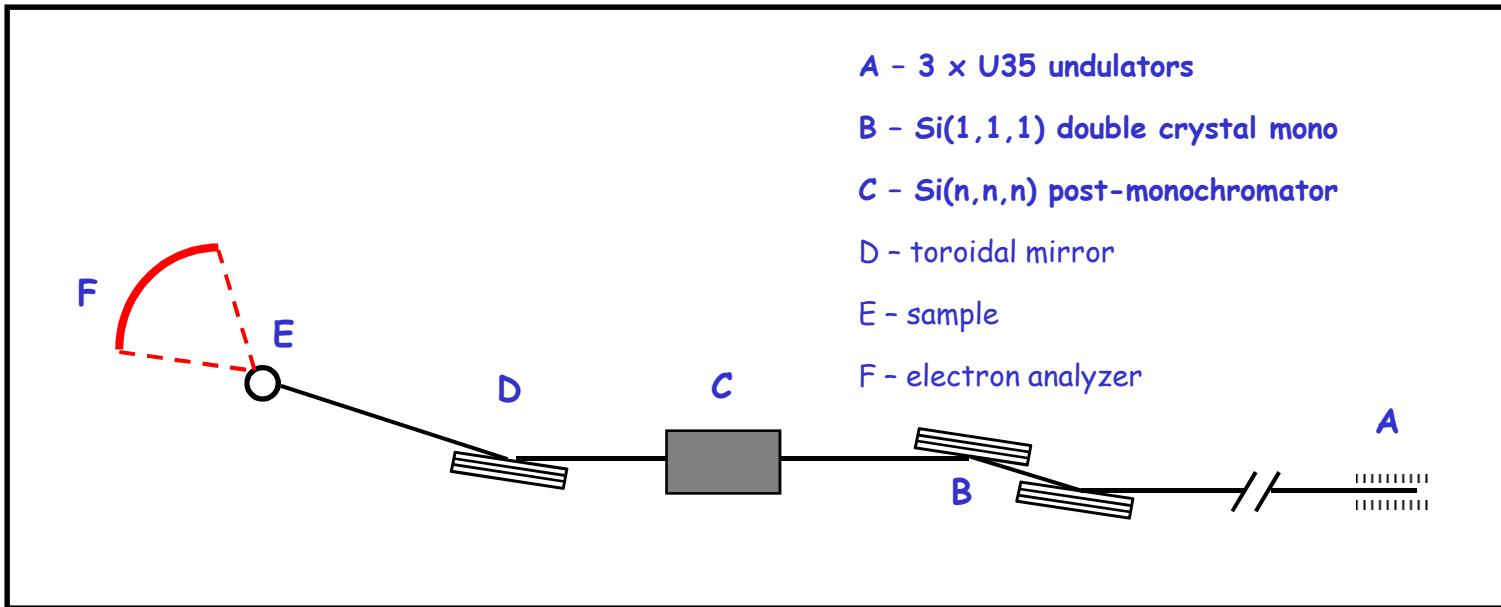
Energy resolution down to < 50 meV

### Needs

- 1) High Res/High flux beamline (low cross sections)
- 2) Adapted Spectrometer performances (high stability/low noise)  
(no commercial equivalent in 2001)

# High Resolution /High Flux beamline

## ID16@ ESRF, inelastic scattering



Channel-cut in backscattering ( $87^\circ$ )

(3,3,3) @ 6 keV:

$\Delta E = 50$  meV &  $6.2 \cdot 10^{11}$  ph/sec/100 mA

(4,4,4) @ 8 keV:

$\Delta E = 37$  meV &  $7.6 \cdot 10^{11}$  ph/sec/100 mA

(5,5,5) @ 10 keV:

$\Delta E = 14$  meV &  $2.6 \cdot 10^{11}$  ph/sec/100 mA

Combination of higher reflection order  
Channel-cut

e.g. (2,2,0) @ 6 keV:

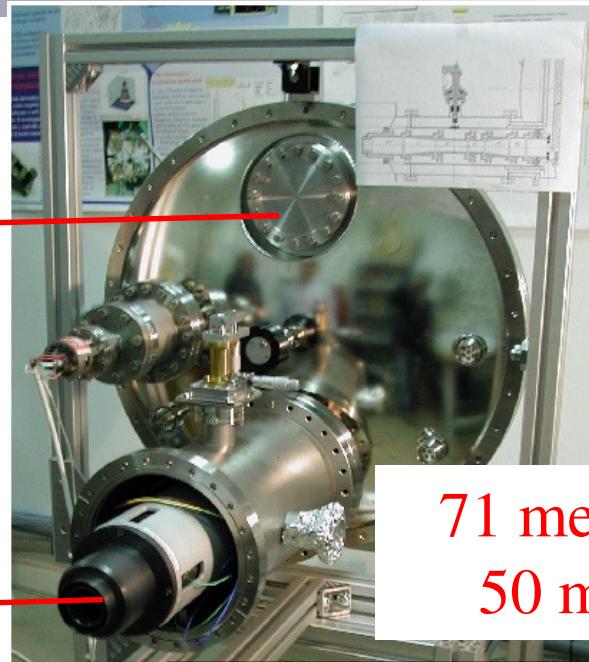
$\Delta E = 340$  meV &  $3 \cdot 10^{12}$  ph/sec/100 mA

Tunable photon energy

# VOLPE's spectrometer

**MB SCIENTIFIC AB**

Dispersive element



+  
(Univ. Rome III and INFM)

Input lens

High retarding factor

Constant linear mag.

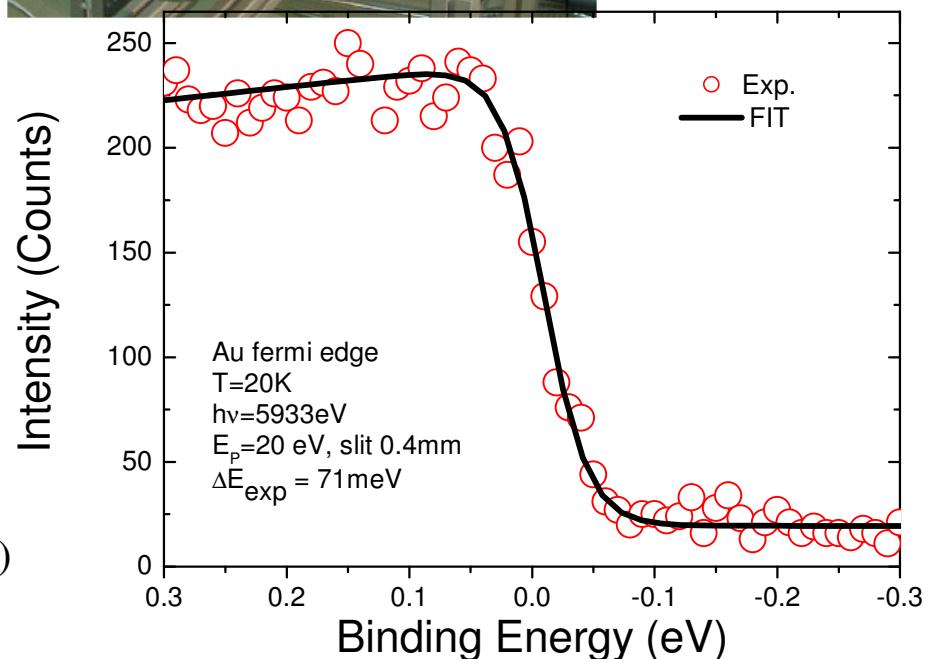
Small field of view

+  
(ELETTRA)

2D delay line detector

High stability power supplies

71 meV @ 5933 eV  
50 meV analyser



P. Torelli *et al.* Rev. Sci. Instr. 76, 023909 (2005)

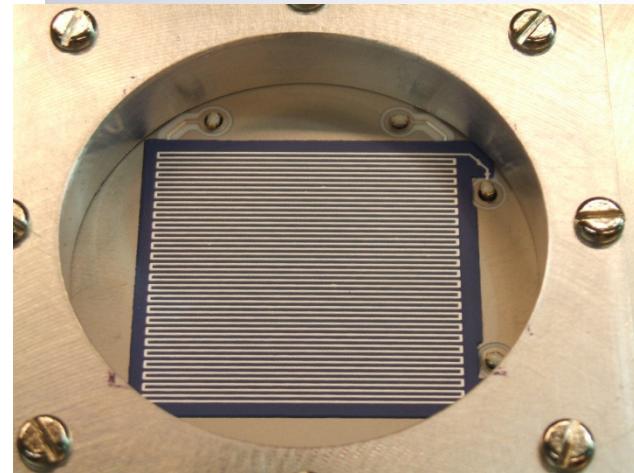
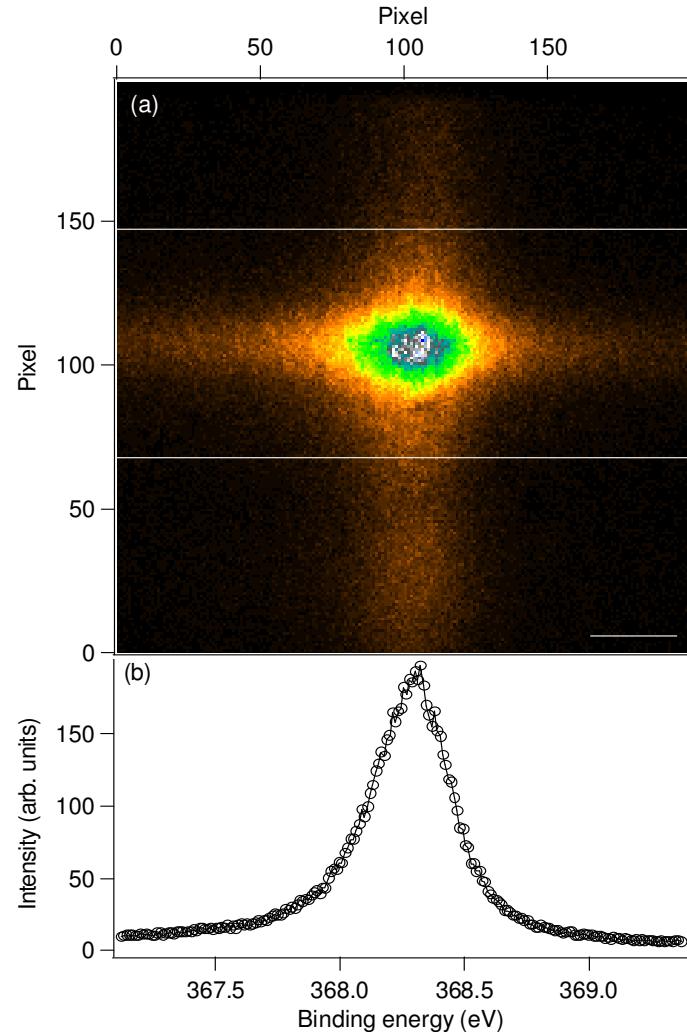
F. Offi *et al.* NIM A, 550, 454 (2005)

G. Panaccione *et al.* NIM A 547, 56 (2005)

# 2D cross delay anode (ELETTRA)

G. Cautero *et al.* NIM A 595, 447 (2008)

P. Torelli *et al.* Rev. Sci. Instr. 76, 023909 (2005)



Dark counts  
< 0.3 events / (sec \* cm<sup>2</sup>)

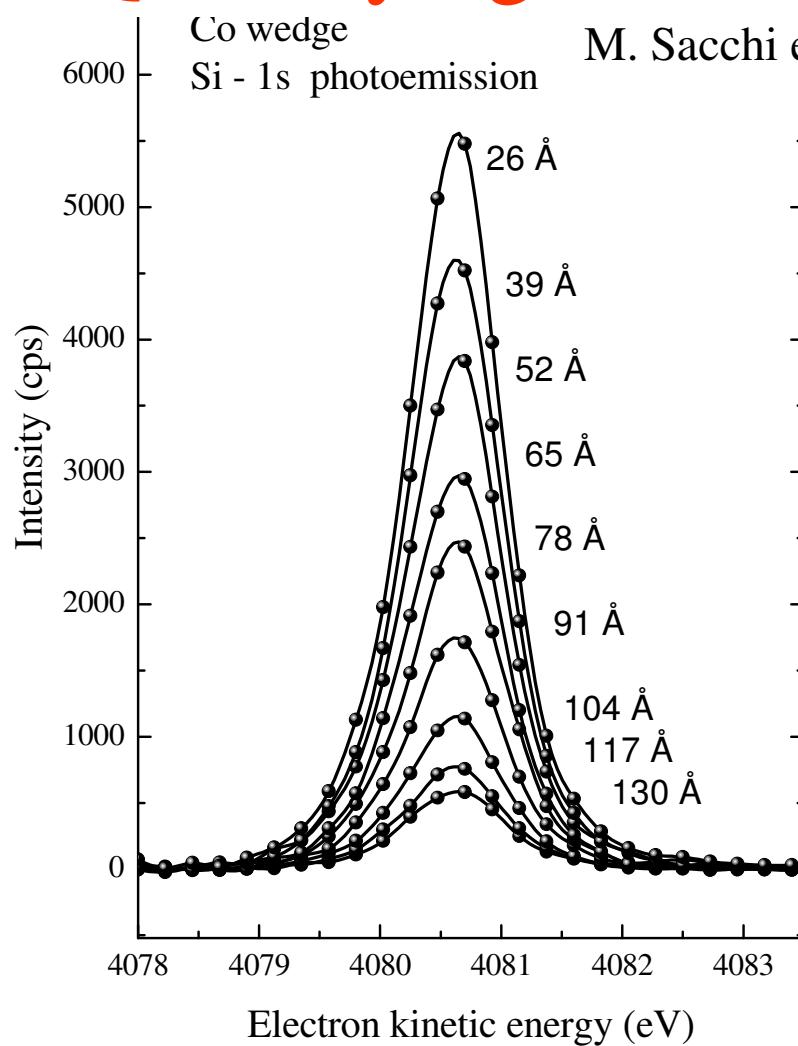
Linearity guaranteed

Decoupling up to 12 kV

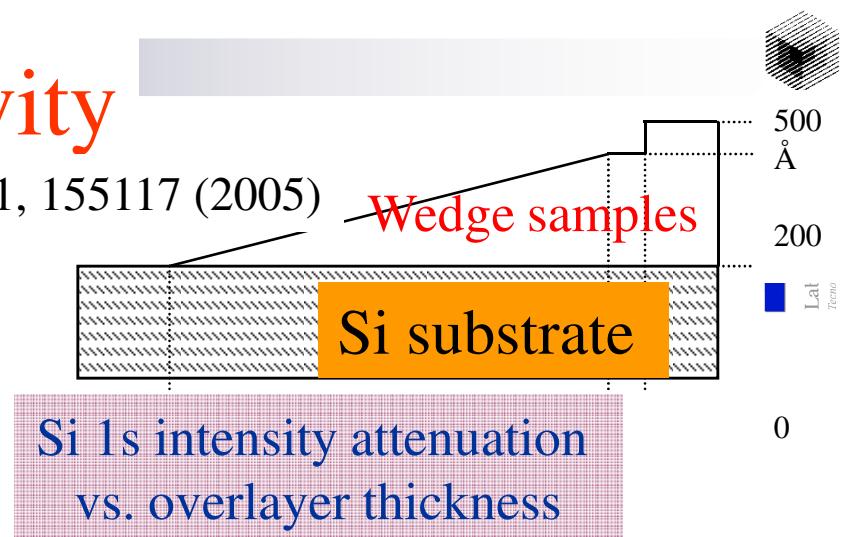
## Technical parameters

- Time resolution: 27ps
- Spatial resolution: <70μm
- Pulse pair resolution: <10ns (multihit capability)
- Real time coincidence check @ 2MHz
- Configuration (1D, 2D, single channel)
- Full time resolved information available

# Quantifying bulk sensitivity

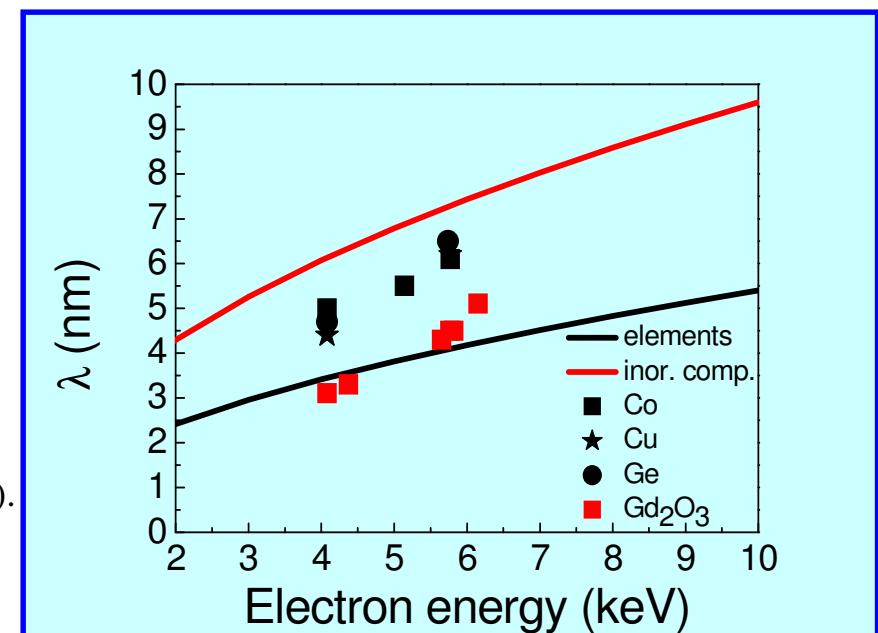


M. Sacchi et al. PRB 71, 155117 (2005)



$$I(x) = I_0 e^{-x/\lambda}$$

Mind the rare-earths!!!!



Jablonski and C.J. Powell, J. El. Spectr. Relat. Phen. 100, 137 (1999).

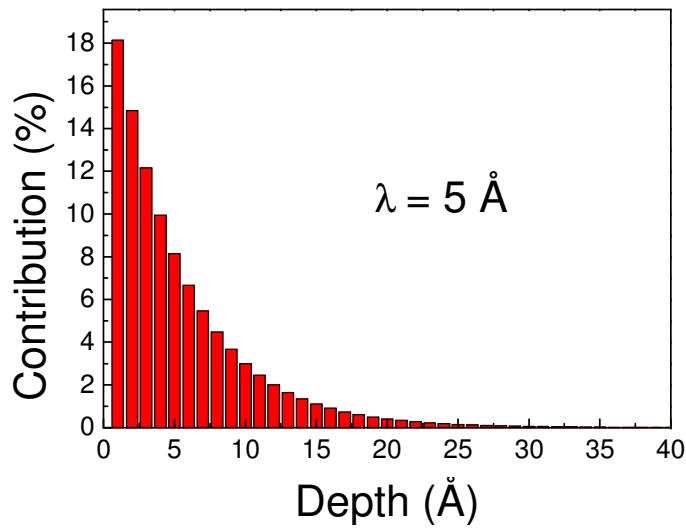
S. Tanuma et al. Surf. Interface Anal. 35, 268 (2003)

M. P. Seah and W. A. Dench, Surf. Interface Anal. 1, 2 (1979)

# Quantifying bulk sensitivity: contribution of the surface

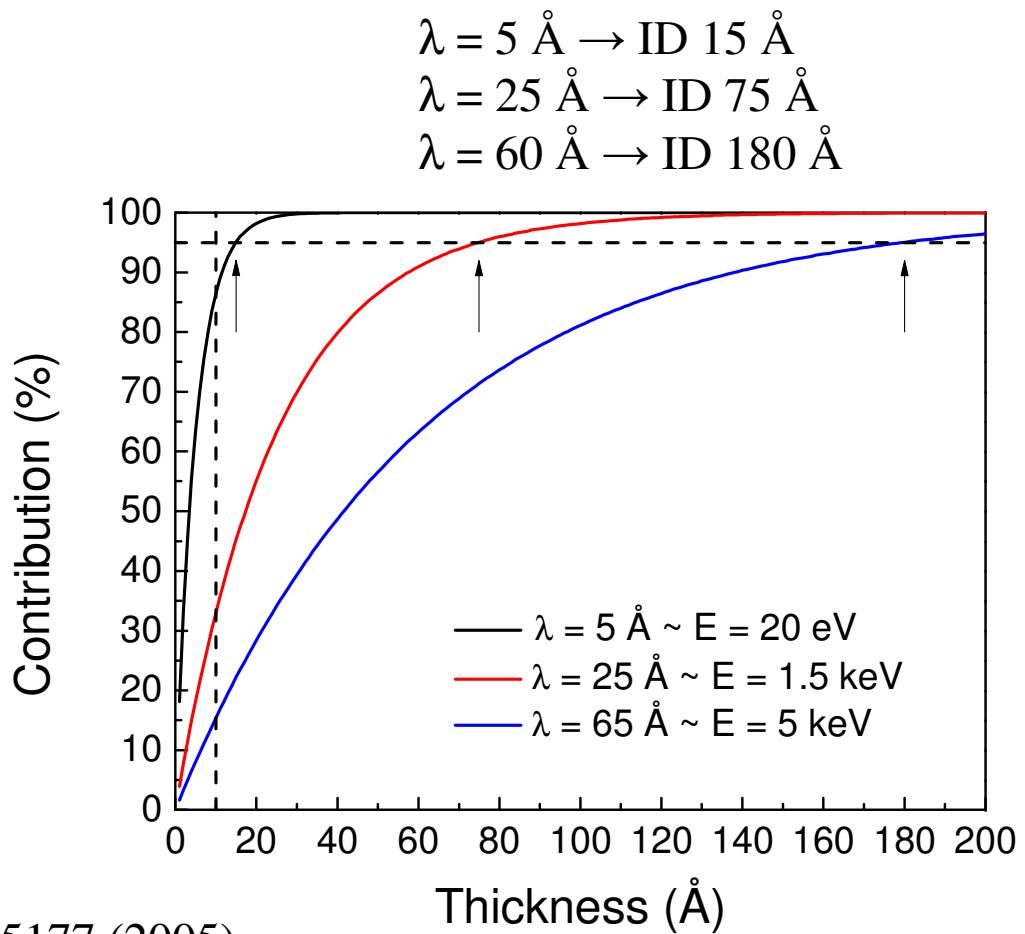
Information depth (ID)

(layer thickness from which 95% of the total signal is produced):



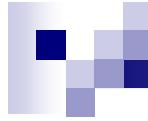
$$\lambda = 5 \text{ \AA}$$

$$I(x) = e^{-\frac{x}{\lambda}}$$



M. Sacchi *et al.*, Phys. Rev. B **71**, 155177 (2005)

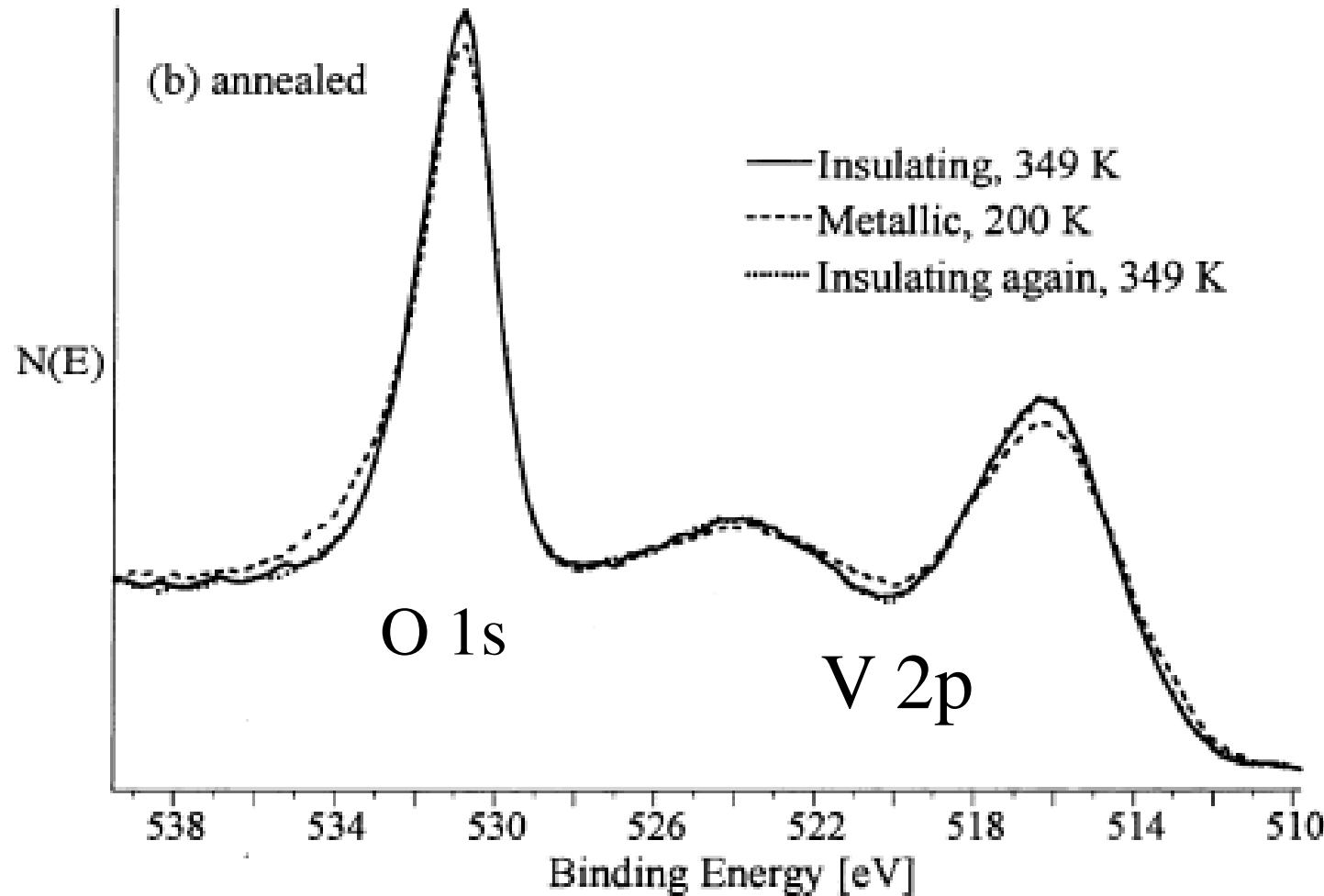
F. Offi *et al.*, Phys. Rev. B **77**, 201101 R (2008)



## Why bulk sensitivity with HAXPES?

### 1. MIT in $\text{V}_2\text{O}_3$

$h\nu = 1253 \text{ eV}$ , small transfer of spectral weight  
despite MIT turns samples into powder

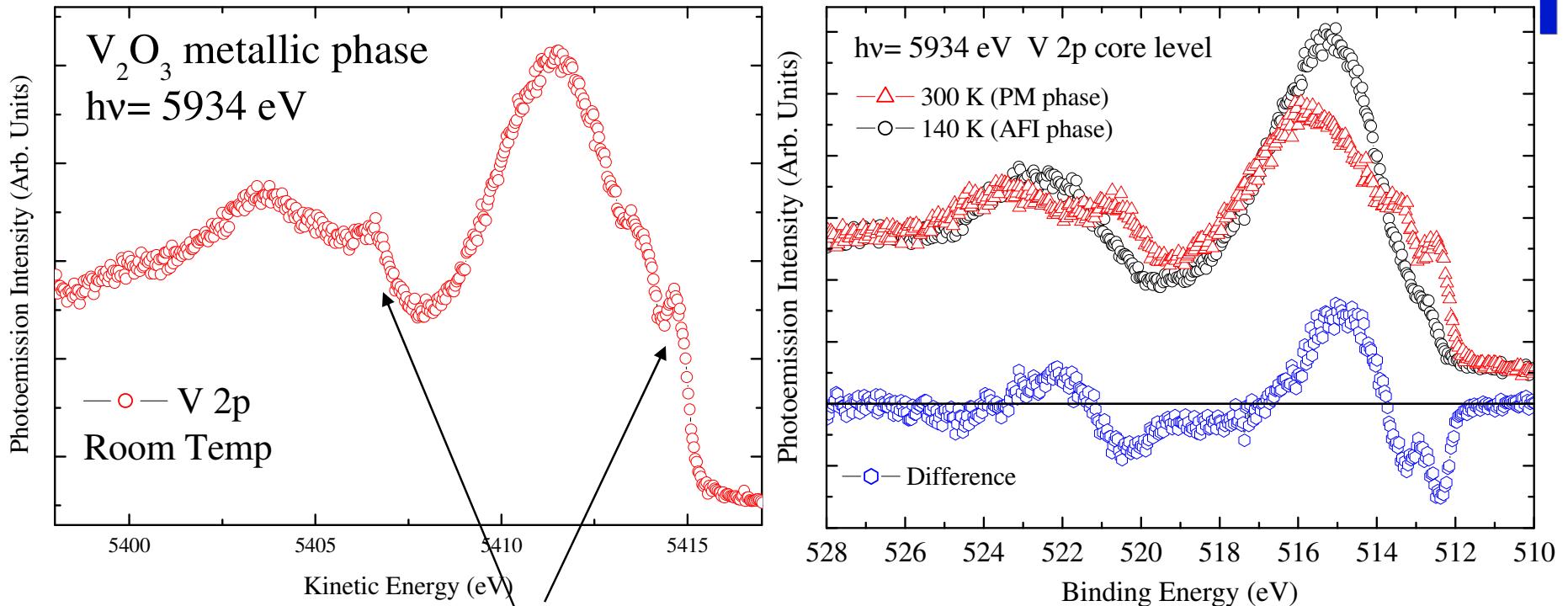


D.S. Toledano et al., Surf. Science 449, 19 (2000)

# MIT in $\text{V}_2\text{O}_3$ with HAXPES: V 2p core level

G. Panaccione et al,  
PRL 97, 116401 (2006)

Extra peaks disappear when crossing the MIT - Huge transfer of spectral weight



Presence of 'extra-peaks' (well screened features)

**only** in bulk sensitive PES., **only** in metallic phase

$\text{V}_2\text{O}_3$ , agreement M. Taguchi et al. PRB 71, 155102 (2005)

M. Taguchi et al. PRL 95, 177002 (2005) G. Panaccione et al. PRB 77, 125133 (2008) NCCO  
K. Horiba et al. PRL 93, 236401 (2004) F. Offi et al. PRB 77, 174422 (2008) Manganites  
Suga's group VO<sub>2</sub>, CrO<sub>2</sub> and many other systems

## Why bulk sensitivity with HAXPES?

### 2. Ruthenates:

Well screened features visible already in the soft X-ray range  
**BUT**  
 Do Surface and Bulk behave identically?

M. Uruma et al. Suga's group  
 arXiv:0711.2160v1 [cond-mat.str-el]

Contribution to PES  
 - Surface  
 - Subsurface  
 - Bulk

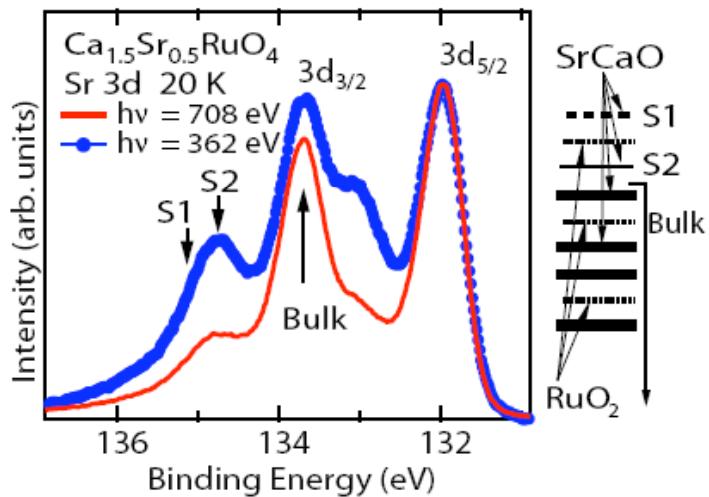


FIG. 1: (color online) Left panel:  $h\nu$  dependence of the Sr 3d core-level PES spectra of  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{RuO}_4$  with the energy resolution of 200 meV. The spectra are normalized at the  $3d_{5/2}$  main peak. The dots with line and solid line correspond to  $h\nu = 362$  eV and 708 eV. Right panel: schematic picture of atomic layers. Strong surface contribution is expected from top-most SrCaO surface layer (S1) and the second SrCaO surface layer (S2) placed just below the top  $\text{RuO}_2$  layer.

# Hard X-ray PES: Surface contribution strongly suppressed

VOLPE @ normal emission  
Almost single line – better spectral purity

Sekiyama et al. PRB 70, 060506(R) 2004

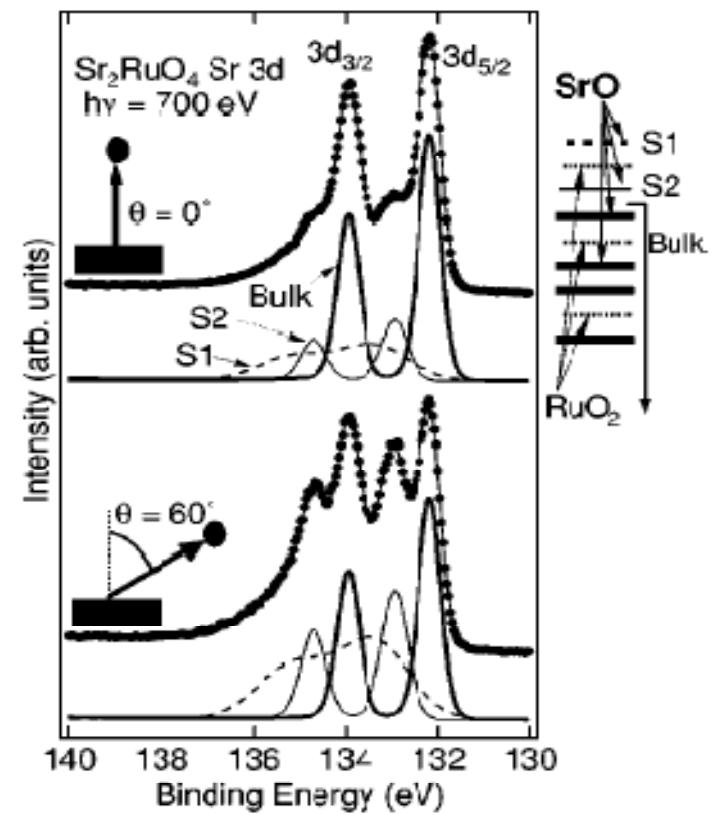
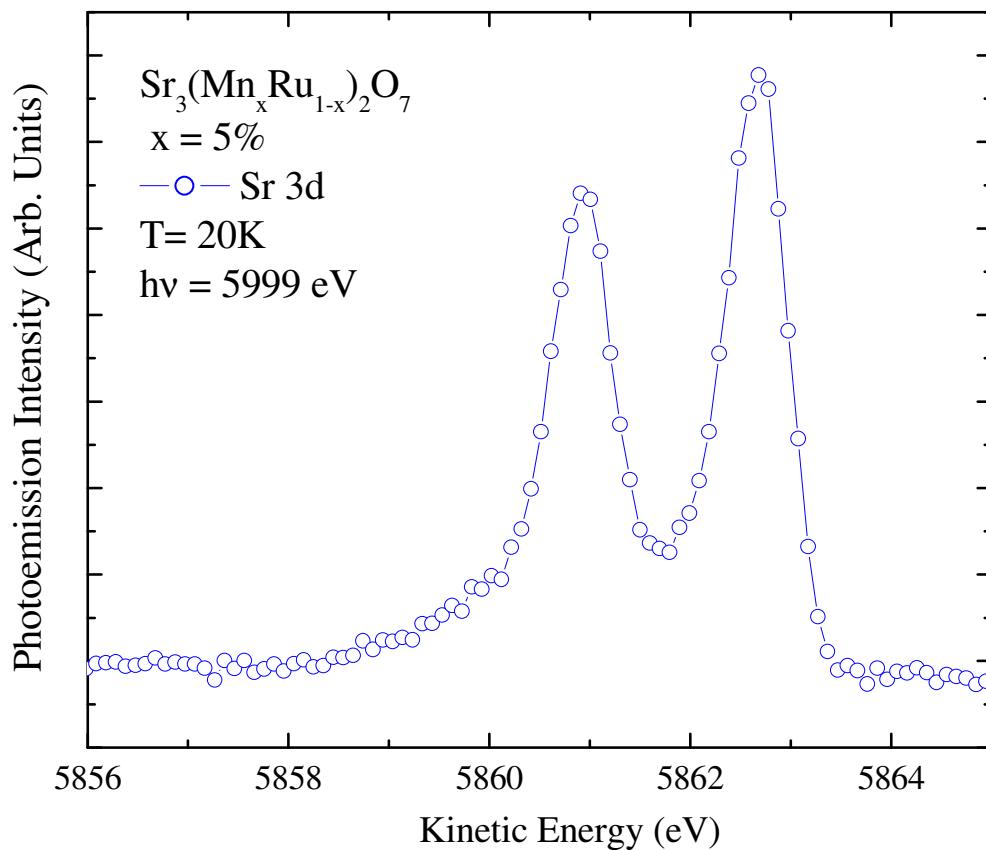
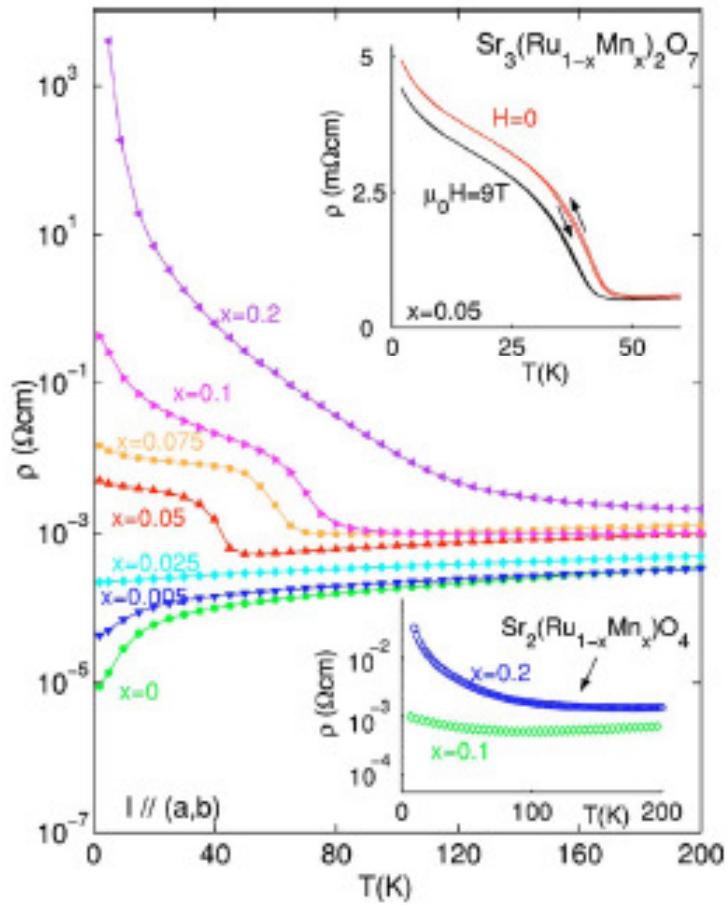


FIG. 1. Polar-angle ( $\theta$ ) dependence of the Sr 3d core-level photoemission spectra of  $\text{Sr}_2\text{RuO}_4$  (filled circles). The spectra are well

# Impurity-induced transition to a Mott insulator in $\text{Sr}_3\text{Ru}_2\text{O}_7$

R. Mathieu,<sup>1,\*</sup> A. Asamitsu,<sup>1,2</sup> Y. Kaneko,<sup>1</sup> J. P. He,<sup>1</sup> X. Z. Yu,<sup>1</sup> R. Kumai,<sup>3</sup> Y. Onose,<sup>1</sup> N. Takeshita,<sup>3</sup> T. Arima,<sup>1,4</sup> H. Takagi,<sup>3,5,6</sup> and Y. Tokura<sup>1,3,7</sup>



Mn substitutes Ru  
Interplay Ru 4d - Mn 3d

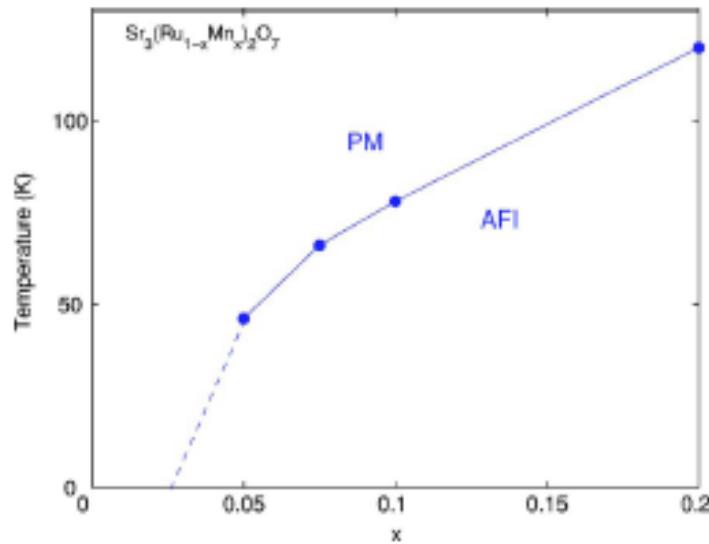


FIG. 4. (Color online) Electronic phase diagram showing the phase boundary between the paramagnetic metal (PM) and antiferromagnetic insulator (AFI) regions. The boundary is plotted using transport data from Fig. 1.

## Crystal-Field Level Inversion in Lightly Mn-Doped Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub>

M. A. Hossain,<sup>1</sup> Z. Hu,<sup>2</sup> M. W. Haverkort,<sup>2</sup> T. Burnus,<sup>2</sup> C. F. Chang,<sup>2</sup> S. Klein,<sup>2</sup> J. D. Denlinger,<sup>3</sup> H.-J. Lin,<sup>4</sup> C. T. Chen,<sup>4</sup> R. Mathieu,<sup>5</sup> Y. Kaneko,<sup>5</sup> Y. Tokura,<sup>5</sup> S. Satow,<sup>6</sup> Y. Yoshida,<sup>7</sup> H. Takagi,<sup>6</sup> A. Tanaka,<sup>8</sup> I. S. Elfimov,<sup>1</sup> G. A. Sawatzky,<sup>1</sup> L. H. Tjeng,<sup>2</sup> and A. Damascelli<sup>1,\*</sup>

Mn 3<sup>+</sup> acceptor  
 Extra e<sub>g</sub> occupies dx<sup>2</sup>-y<sup>2</sup>  
 3d-4d interplay responsible of MIT with AFI order (possible OO)

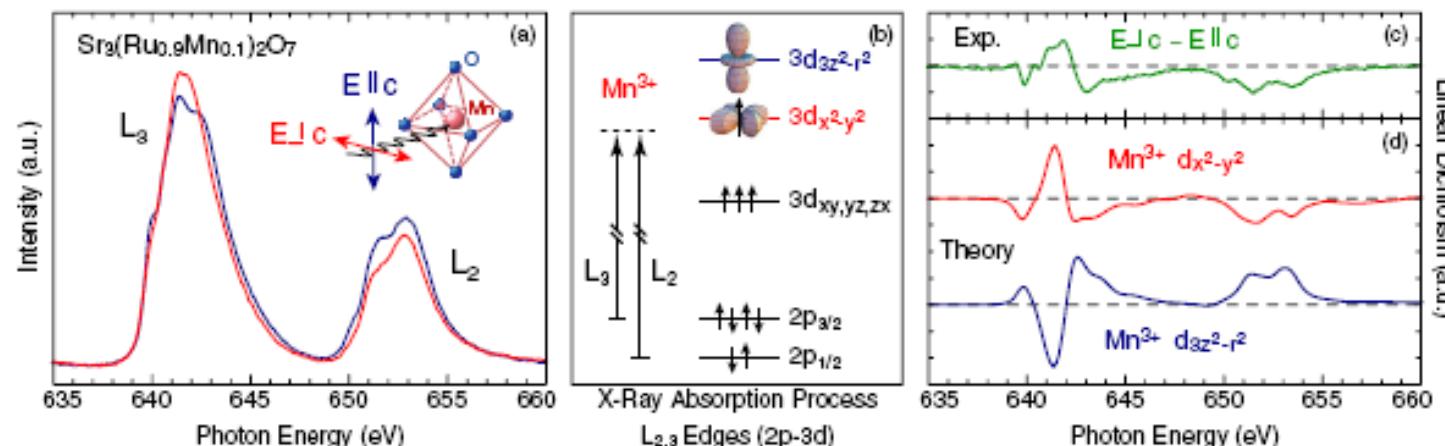


FIG. 2 (color online). (a) Polarization-dependent Mn  $L_{2,3}$ -edge XAS spectra from  $\text{Sr}_3(\text{Ru}_{0.9}\text{Mn}_{0.1})_2\text{O}_7$  at  $T = 295$  K. (b) Scheme of the XAS process: the  $L_2$  ( $L_3$ ) edge corresponds to the excitation of a  $\text{Mn} 2p_{1/2}$  ( $2p_{3/2}$ ) electron to the  $\text{Mn} 3d$  valence shell. The  $L_3 - L_2$  energy separation is due to the  $2p$  core level spin-orbit coupling. (c) Corresponding experimental linear dichroism (LD), defined as  $\text{LD} = [I_{\text{XAS}}(E \perp c) - I_{\text{XAS}}(E \parallel c)]$ . (d) Calculated LD spectra for two possible  $e_g$ -orbital occupations ( $x \parallel a$ ,  $y \parallel b$ ,  $z \parallel c$ ).

# Sr<sub>3</sub>(Mn<sub>x</sub>Ru<sub>2-x</sub>)O<sub>7</sub>: Evolution vs. doping? Surface vs bulk? Direct access to Ru with core level PES

Extra peaks due to competition  
between local and non local screening

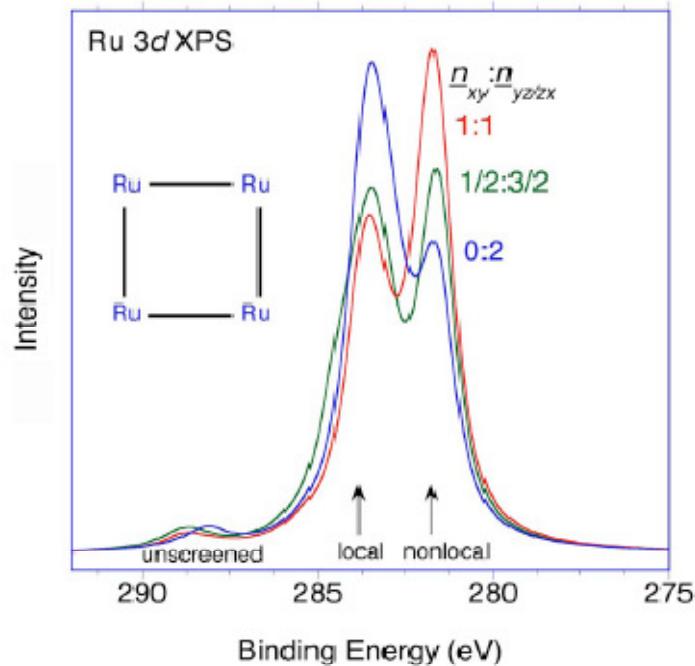


FIG. 5. (Color online) Ru 3d XPS line shapes for a Ru<sub>4</sub> cluster for different orbital occupations. The ratio between the  $n_{xy}$  and  $n_{yz/zx}$  holes is varied by introducing an energy difference  $\Delta E$  between the  $xy$  and  $yz/zx$  orbitals. Spectra are given for  $n_{xy}:n_{yz/zx}=1:1, \frac{1}{2}:\frac{3}{2}$ , and 0:2 for  $\Delta E=0.01, 0$ , and  $-0.32$  eV, respectively.

M.A. Van Veenendaal, Phys. Rev. B 74, 085118 (2006)

M.A. Van Veenendaal and G. Sawatzky PRL 70, 2459 (1993)

Chainani and Taguchi talks

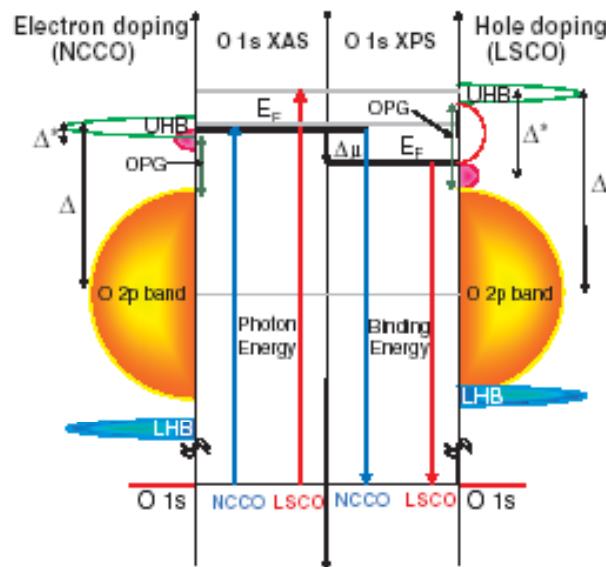


FIG. 4 (color). Schematic illustration of the energy levels of LSCO and NCCO obtained from the IAM analysis. OPG represents the optical gap in undoped materials. The Fermi level ( $E_F$ ) separates the occupied density of states (shaded regions) from the unoccupied density of states.

M. Taguchi et al. PRL 95, 177002 (2005)

A. Kotani and K. Okada,  
J. Phys. Soc. Jpn. 74, 653 (2005)

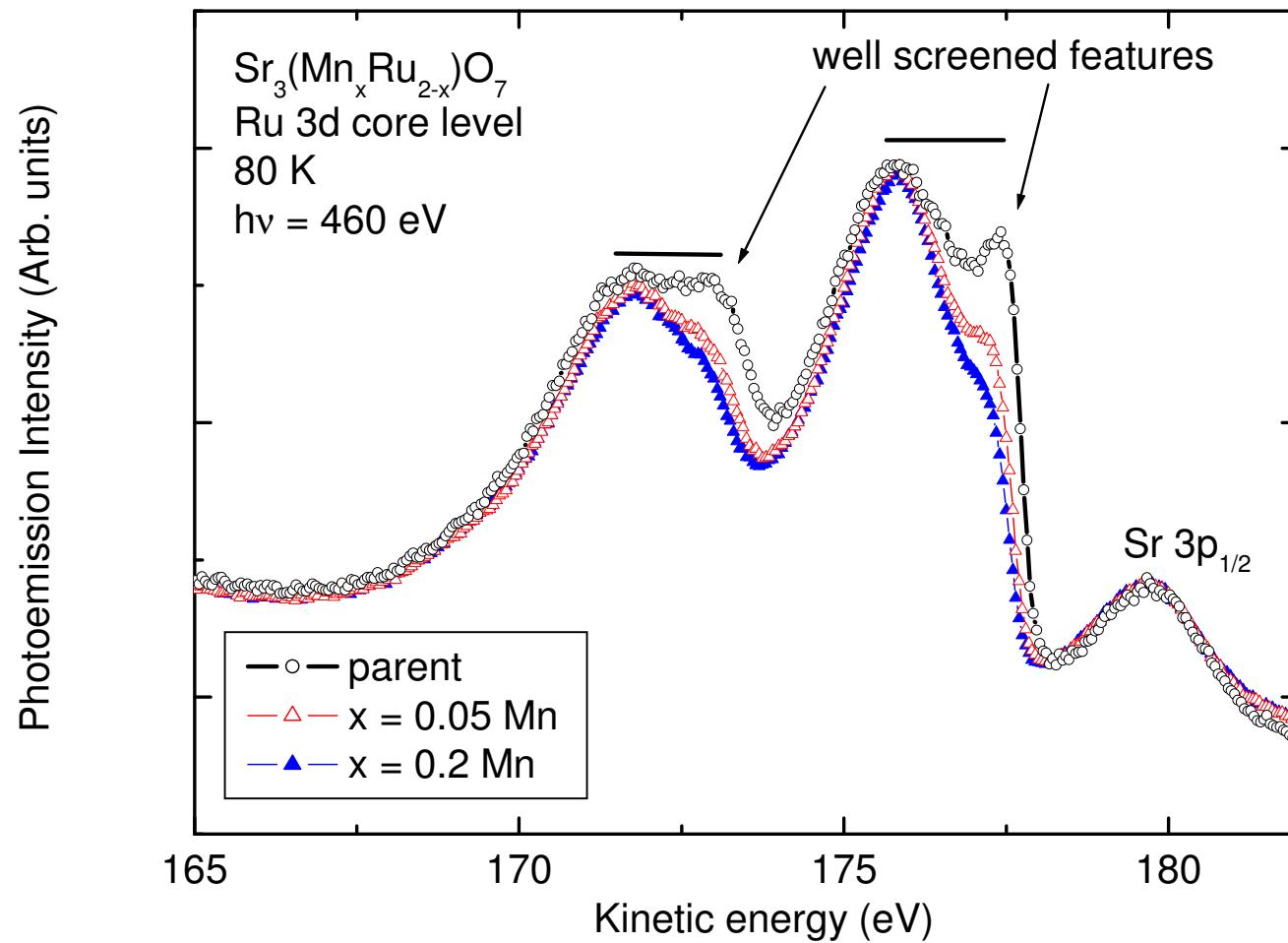
# Satellite peaks in TMO core levels: soft X-rays

Clear doping dependence in the screening channels

APE beamline, ELETTRA

E. Annese, GP et al.

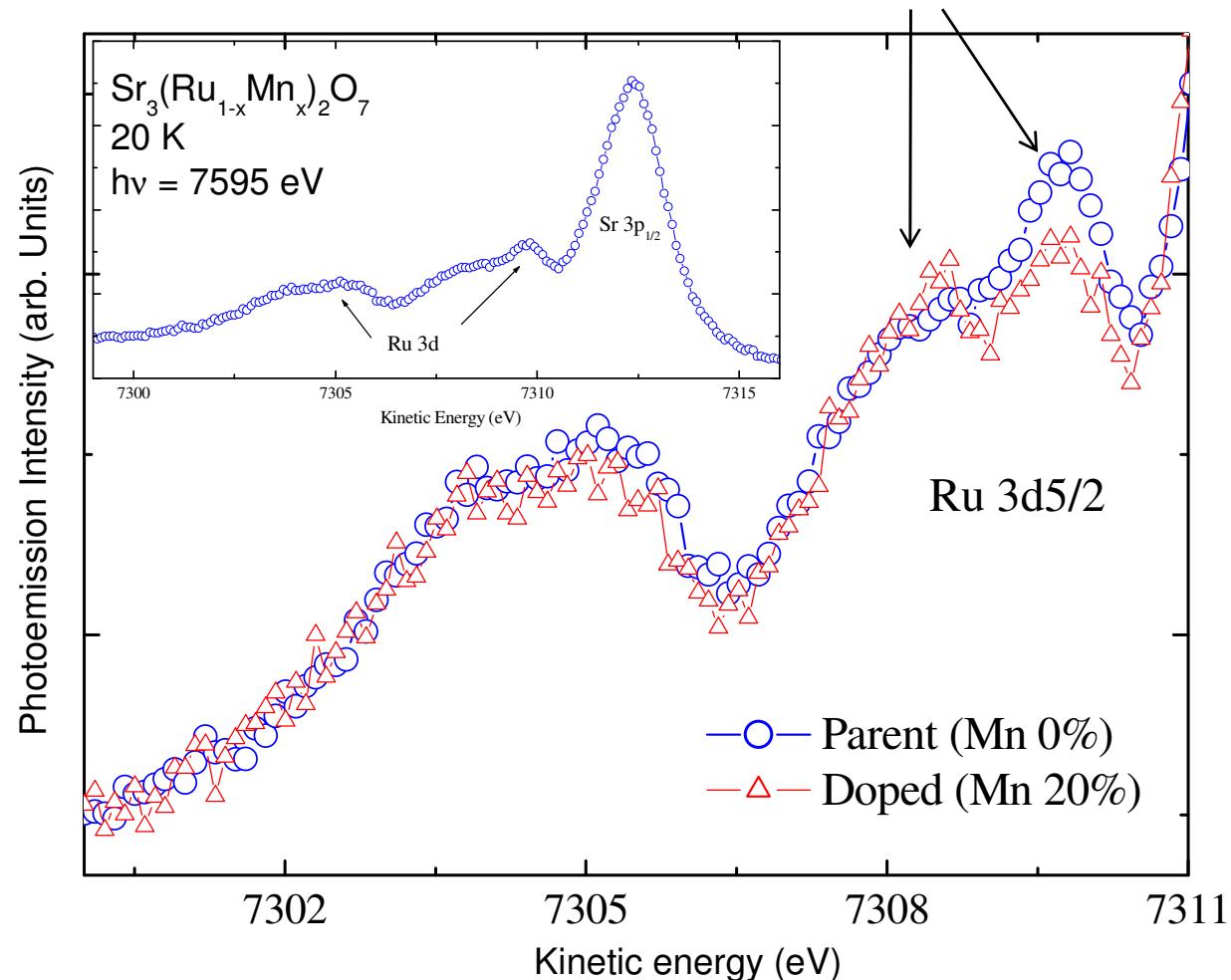
NORMAL EMISSION 45 DEGREE INCIDENCE



In collaboration with A. Damascelli, G. Sawatzky, UBC, Vancouver, Canada

# Satellite peaks in TMO core levels: Hard X-rays

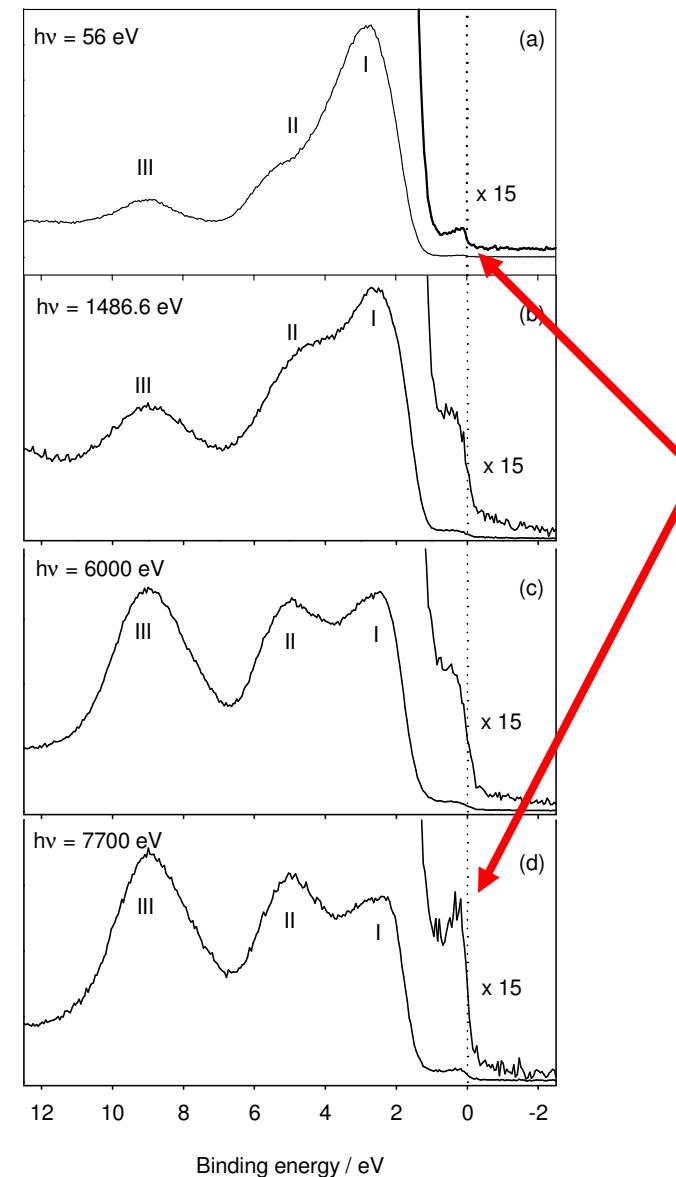
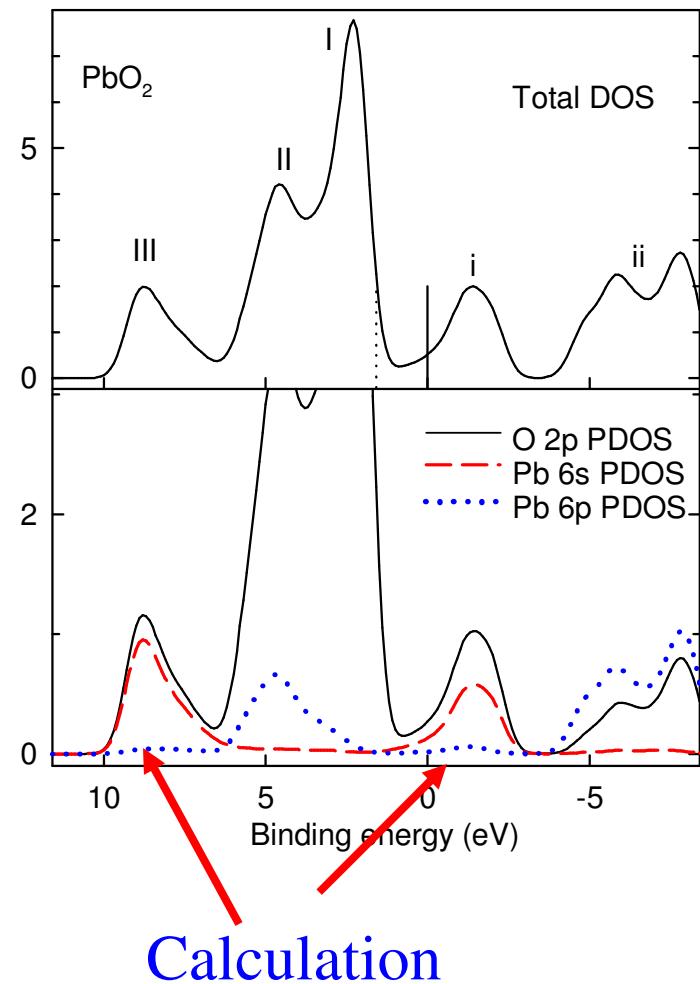
Evolution vs. doping confirmed  
BUT  
Different ratio well screened/main peaks

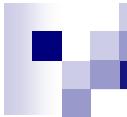


# Enhancing s-contribution with HaXPEES: Fermi level in Lead Dioxide ( $\beta$ -PbO<sub>2</sub>)

D.J. Payne, R.G. Egdell, et al. PRB **75**, 153102 (2007)

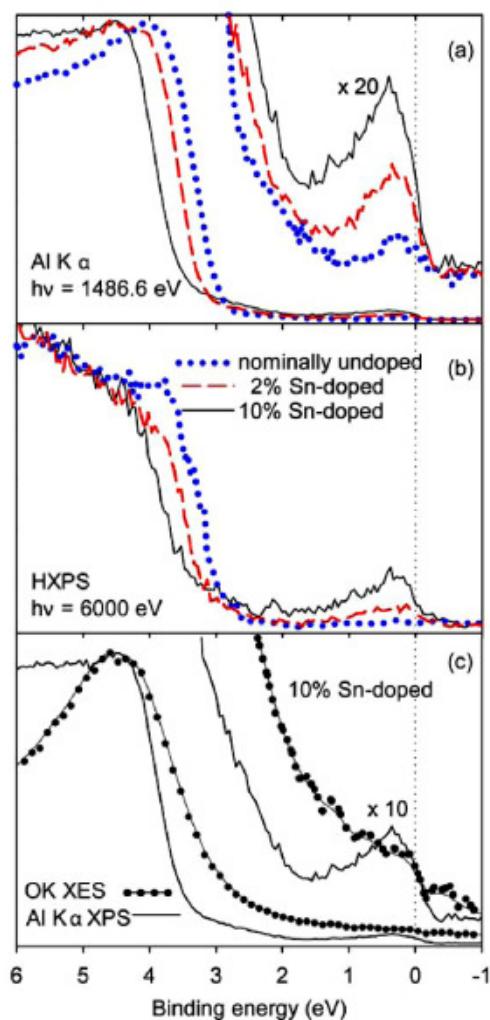
D.J. Payne, et al J. Phys. C, in press





## Nature of the Band Gap of $\text{In}_2\text{O}_3$ Revealed by First-Principles Calculations and X-Ray Spectroscopy

A. Walsh et al, PRL 100, 167402 (2008)



Evolution of the s-like intensity  
at Fermi level vs. Sn doping

Combination of XES and HaXPEs

Failure of band bending model

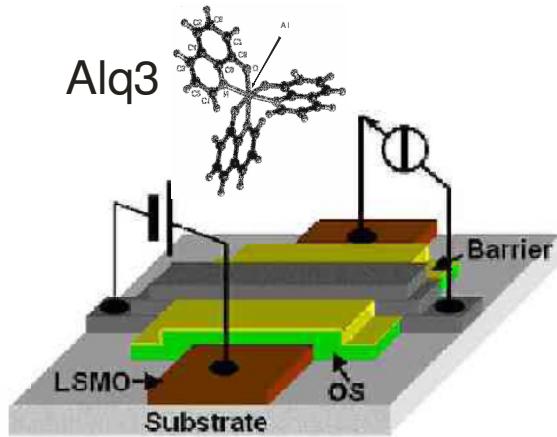
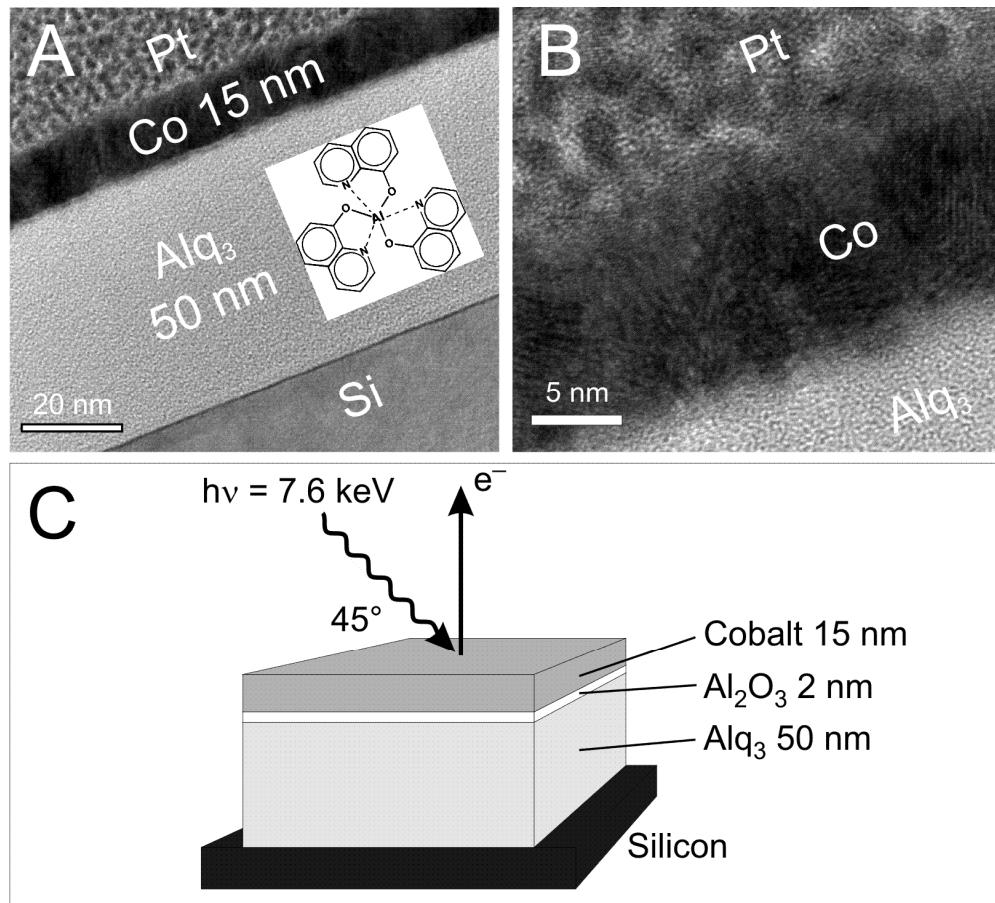
Upper limit 2.9 eV instead of 3.75 eV

Revision needed for interface band offset,  
e.g.  $\text{In}_2\text{O}_3/\text{Si}$  will be  $< 1$  eV

FIG. 1 (color online). (a) Al K $\alpha$  XPS ( $h\nu = 1486.6$  eV) of nominally undoped and 2% and 10% Sn-doped  $\text{In}_2\text{O}_3$  thin films. (b) HXPS ( $h\nu = 6000$  eV) of the same films. (c) Al K $\alpha$  XPS and O K shell XES of 10% Sn-doped  $\text{In}_2\text{O}_3$  aligned using the Fermi edge (0 eV) visible in both spectra.

# Buried interfaces with HaXPEES: Organic spin valve - (LSMO-Alq<sub>3</sub>)

TEM, J. Chapman, Univ. Glasgow, UK



Epitaxial LSMO (20 nm) film  
Alq<sub>3</sub> spin/charge layer (50-100 nm),  
Thin tunnel barrier (AlO<sub>x</sub> 1-2 nm)  
Co top electrode (10-20 nm)

Alq<sub>3</sub>(50 nm)/Co(15 nm)  
Alq<sub>3</sub>(50 nm)/AlO<sub>x</sub>(2 nm)/Co(15 nm).

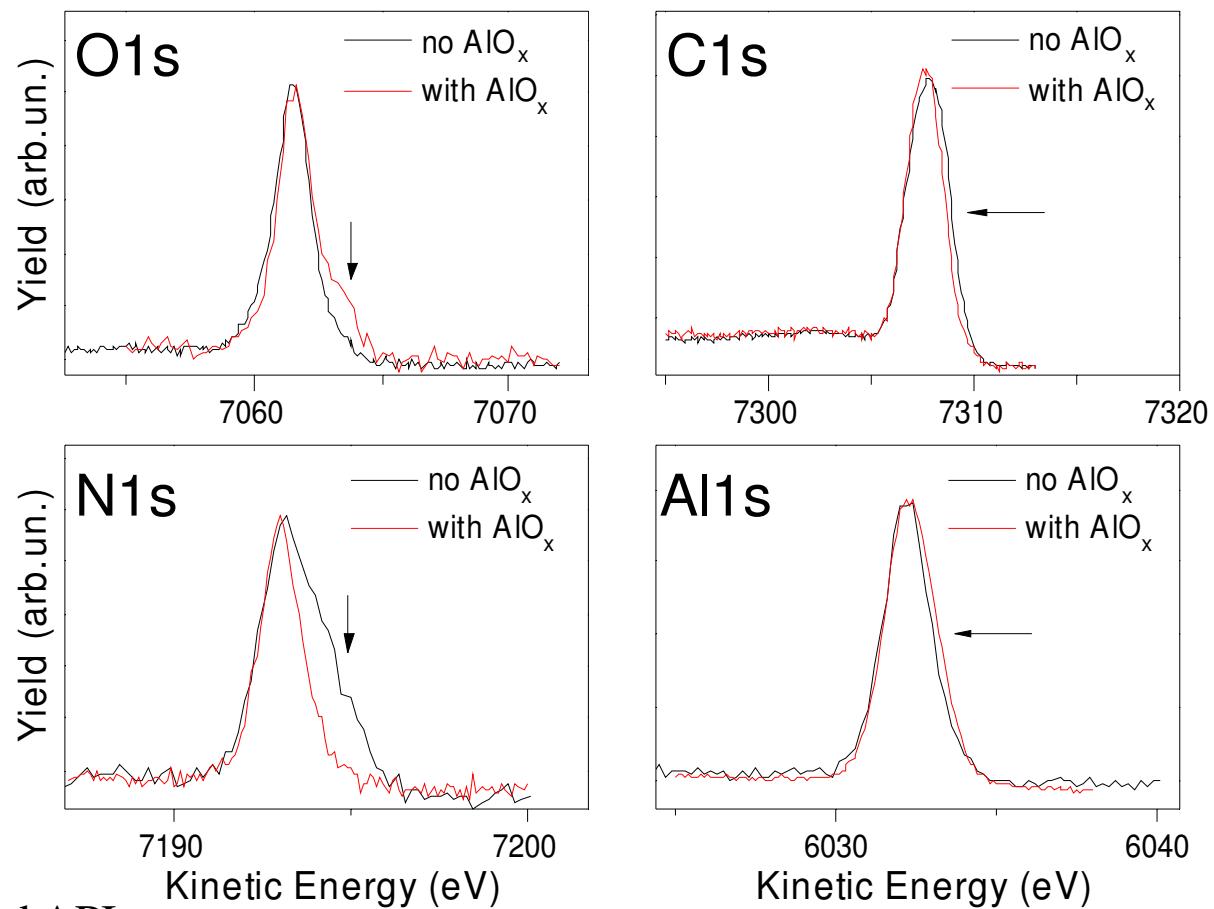
# Buried interfaces with HaXPE:

## Organic spin valve - (LSMO-Alq3)

Core-level of Alq<sub>3</sub>/Co interface  
without (black) and with (red) presence of AlO<sub>x</sub> film (1-2 nm)

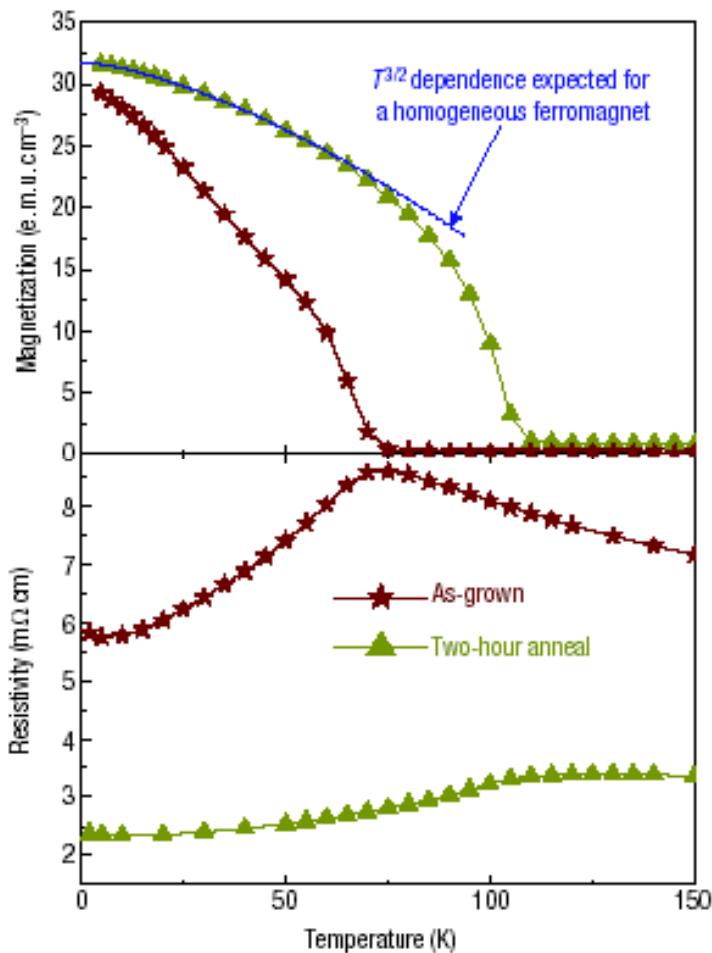
As-grown samples

15 nm capping

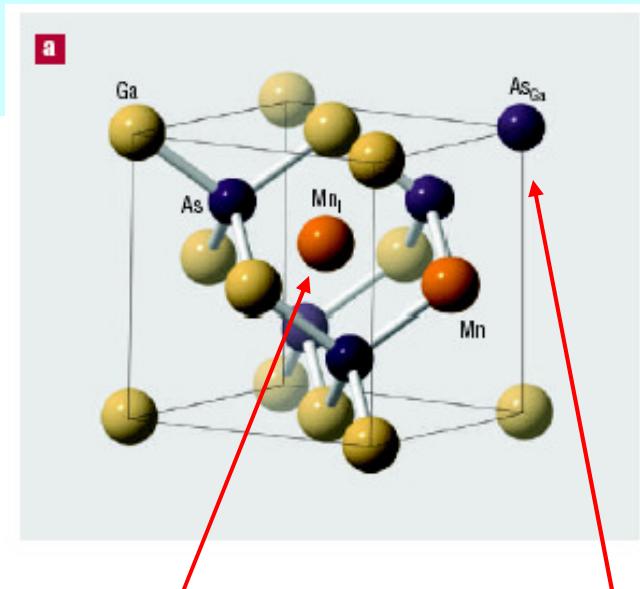


# Doping control: Ferromagnetic Semiconductors

## Model system: $\text{Ga}_{1-x}\text{Mn}_x\text{As}$



**Figure 2** The temperature dependence of the magnetization and resistivity of  $\text{Ga}_{0.985}\text{Mn}_{0.017}\text{As}$  (ref. 36). The two curves in each are for non-annealed (as grown) and annealed samples, and they reveal the striking physical changes wrought by annealing (increased  $T_c$  and conductivity, and conventional behaviour of the temperature-dependent magnetization).



Low T growth = Mn interstitial + As antisites  
 Post annealing  $T_c \uparrow$  conductivity  $\uparrow$

BUT

$T_c \downarrow$  if thickness  $\uparrow$   
 Surface vs. bulk magnetic properties  
 $T_c < 200$  K

A.H. Macdonald,  
 Nature Mat. 4, 195 (2005)

## Convincing a magnetic semiconductor to work at room temperature

Charles Gould and Laurens W. Molenkamp

Published December 22, 2008

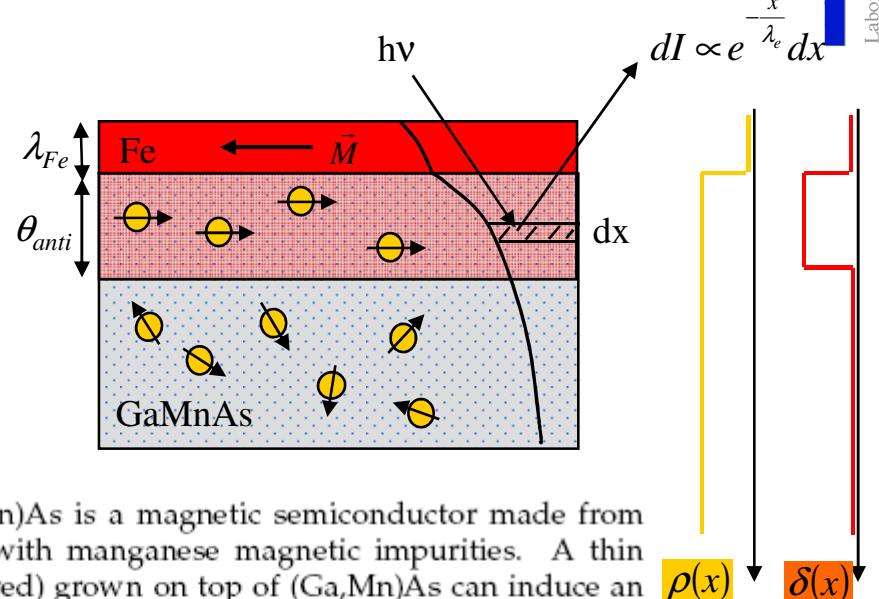
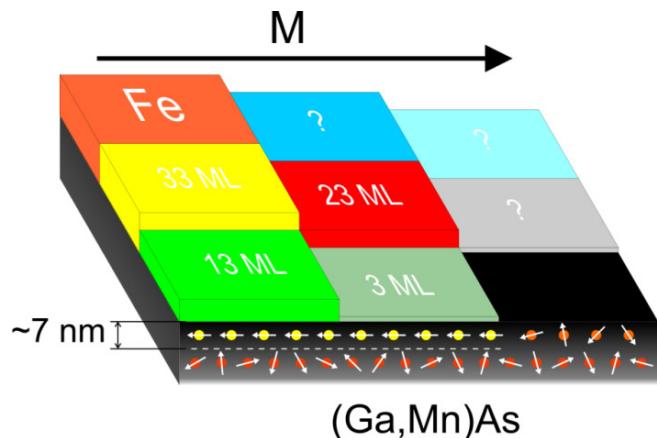
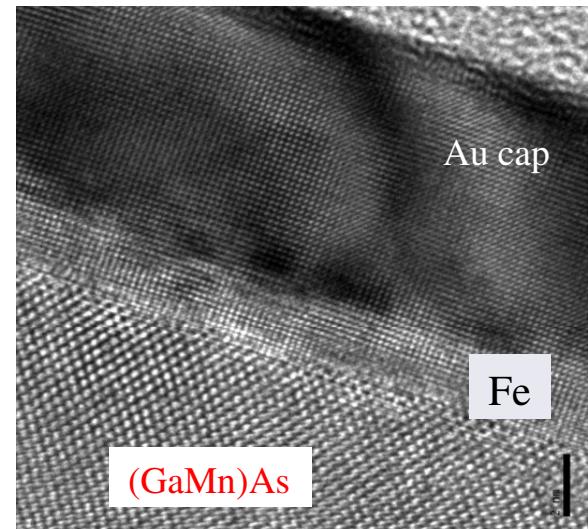
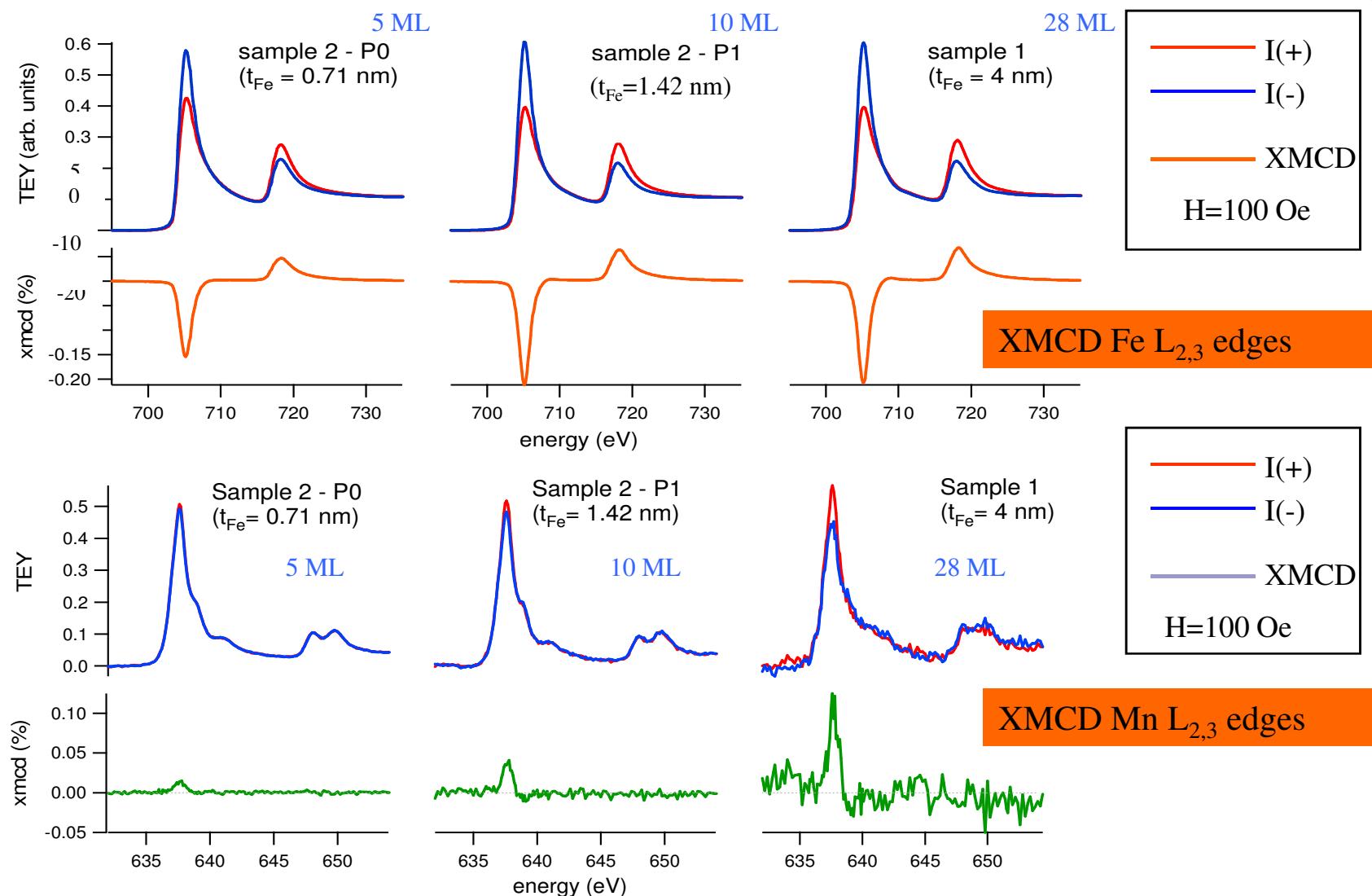


FIG. 1:  $(\text{Ga},\text{Mn})\text{As}$  is a magnetic semiconductor made from  $\text{GaAs}$  doped with manganese magnetic impurities. A thin layer of iron (red) grown on top of  $(\text{Ga},\text{Mn})\text{As}$  can induce an ordering of the manganese magnetic moments (small black arrows). The magnetic order extends over a layer across the interface (middle, yellow) and the induced magnetization is opposite to that of the iron ( $M$ ). The magnetization of the interfacial layer persists even at room temperature, when the bulk of the  $(\text{Ga},\text{Mn})\text{As}$  is paramagnetic. (Illustration: Alan

Collaboration with:  
Prof. W. Wegscheider (Univ. of Regensburg)  
Prof. C. H. Back (Univ. of Regensburg)  
Prof H. Ebert, (LMU, Muenchen)

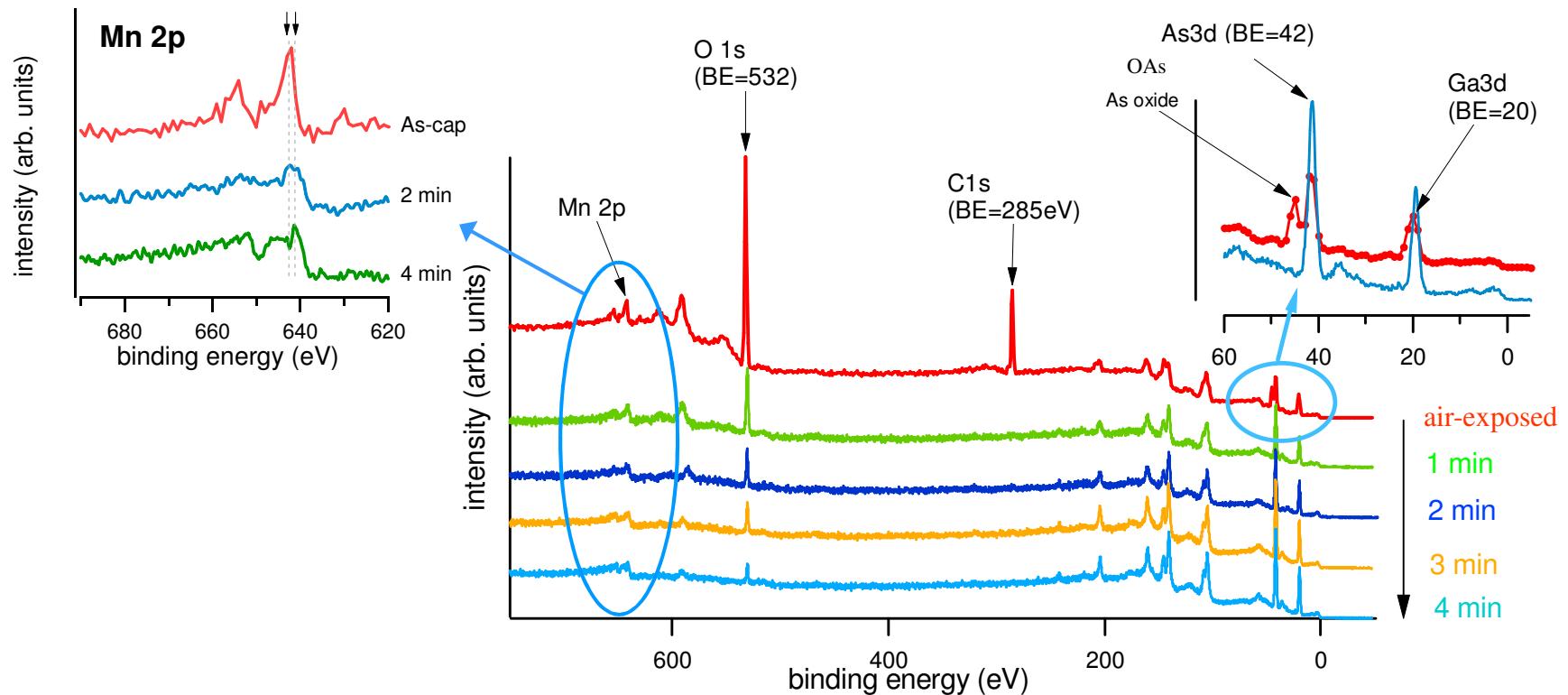
# Magnetic coupling: XMCD at Fe and Mn L<sub>2,3</sub> (APE beamline)

Mn layers magnetized anti-parallel to Fe; Mn Ferromagnetic at RT



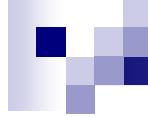
# Fe/(GaMn)As interfaces: next step with HAXPES

**Evolution of Mn 2p core lines vs. Fe Thickness and doping  
In as-grown and capped samples (NO SPUTTERING)**



F. Maccherozzi et al., APE beamline, in preparation

See also B. Schmid, R. Claessen, W. Drube et al. PRB 78, 075319 (2008)



## Examples of ‘useful’ HAXPES experiments

- Surface properties different from the bulk  
(and you search for bulk properties , e.g. some TMOs)  
(correlation, reconstruction, high sensitivity to contamination, no easy cleavage plan)
- Surface or interfaces properties different from the bulk  
(and you would like to tailor new interface properties , e.g. Fe/(GaMn)As)
- Buried systems  
(as grown, capped)
- sp contribution at Fermi level and cross section change may be important

Competitive with XAS in TEY

Valence band + core level needed  
Comparison with soft X-ray needed



# Acknowledgements

## VOLPE group and collaborators

ESRF (France), G. Monaco, S. Huotari, A. Fondacaro,  
C. Henriet, L. Simonelli

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